

MELT SPINABLE CONCENTRATE PELLETS HAVING ENHANCED  
REVERSIBLE THERMAL PROPERTIES

CROSS-REFERENCE TO RELATED APPLICATIONS

This patent application claims the benefit of copending U. S. provisional  
5 patent application Serial No. 60/234,150, filed September 21, 2000.

This application incorporates by reference the disclosure of the  
following co-pending U.S. provisional patent applications, owned by the  
assignee of the present application: "Melt Spinnable Multi-component Fibers  
Having Enhanced Reversible Thermal Properties," by Monte Magill, Serial No.  
10 60/234,410, filed September 21, 2000 (now non-provisional patent application  
Serial No. \_\_\_\_\_ filed \_\_\_\_\_); and "Thermally Stable Phase Change  
Material For Use In Temperature Regulating Fibers, Fabrics And Textiles," by  
Monte Magill and Mark Hartmann, Serial No. 60/234,149, filed September 21,  
2000 (now non-provisional patent application Serial No. \_\_\_\_\_ filed  
15 \_\_\_\_\_).

BACKGROUND OF THE INVENTION

Field of the Invention:

This invention relates to the manufacture of melt spun synthetic fibers  
having temperature regulation properties, the melt spun fibers being formed  
20 from polymer-based concentrate pellets that have Phase Change Materials  
(PCMs) therein.

Description of the Related Art:

Many fabric materials are made from synthetic fibers. Two processes - -  
a wet solution process and a melt spun process - - are generally used for  
25 making synthetic fibers. The wet solution process is generally used to form  
acrylic fibers, while the melt spun process is used to form nylons, polyesters,

polypropylenes, and other similar type fibers. A large portion of the fibers that are used in the textile industry are made via the melt spun process.

As is well known, nylon is a family of polyamide polymers characterized by the presence of the amide group CONH; polyester fiber is a fiber in which  
5 the fiber-forming substance is a long chain synthetic polymer composed of at least 85-percent by weight of an ester of a dihydric alcohol and terephthalic acid; and polypropylene ( $C_3H_5$ ) is a synthetic crystalline thermoplastic polymer having a molecular weight of about 40,000 or more.

The melt spun manufacturing process generally involves passing a  
10 melted polymeric material or pellets through a device known as a spinneret, to thereby form individual polymeric fibers. The fibers are then made into a filament/strand, or into a cut staple. After the fibers have been formed, the fibers can be used to make non-woven material, or alternatively, the fibers can be wound into a yarn that is comprised of individual fibers, the yarn to be used  
15 thereafter in the weaving or knitting of a fabric material.

In order to provide a thermal regulation property to fabric materials, microencapsulated phase change materials (microPCMs or mPCMs) have been incorporated into acrylic fibers that were made using an aqueous batch (solution) process. However, with respect to synthetic fibers that are made by  
20 the melt spun manufacturing process wherein excessive amounts of volatile materials should not be present, conventional aqueous batch methods for incorporating mPCMs into the fibers are problematic.

It is against this background that embodiments of the present invention were developed.

# SUMMARY OF THE INVENTION

According to one aspect of the present invention, disclosed herein is a process for manufacturing melt spinnable concentrate pellets that contain Phase Change Materials (PCMs), but do not contain an excessive amount of volatile materials. In accordance with this invention, the PCMs can be microencapsulated PCMs that are within the concentrate pellets, the PCMs can be absorbed into carrier polymers that form the concentrate pellets, and/or non-micro-encapsulated PCMs can be included as a component of the concentrate pellets.

10 According to the invention, the melt spinnable concentrate pellet matrix, or carrier polymer, can be any thermoplastic polymer or any combination of thermoplastic polymers.

Concentrate pellets in accordance with the invention, can be blended into similar thermoplastic polymers, and the blend can then be extruded to form monofilament melt spun fibers, extruded films, injection molded products, etc., or the concentrate pellets can be blended with different thermoplastic polymers and the blend can then be extruded to form bicomponent or multi-component melt spun fibers, multi-component extruded films, multi-component injection molded products, etc.

20 For example, polypropylene concentrate pellets that contain PCMs or mPCMs can be blended with an additional amount of the polypropylene polymer and then melt spun to form polypropylene monofilament fibers, or this same polypropylene concentrate pellet can be blended with, or bicomponent melt spun with, an amount of nylon polymer to form bicomponent polypropylene/nylon fibers.

In accordance with a feature of the invention, but without limitation thereto, a PCM(s), and preferably a microencapsulate PCM(s), in a wet-cake form (i.e. in a water-based form) that comprises about 70 weight-percent

solids and about 30 weight percent water, is melt-blended with a low molecular weight dispersing-polymer, with the result that about all of the water that is within the wet cake is driven off as the PCM(s) is concomitantly generally uniformly dispersed throughout the low molecular weight dispersing polymer.

5 In this mixture of a PCM(s) and a low molecular weight dispersing polymer, the dispersing polymer is selected for its compatibility with, and for its affinity for, the PCM(s), thus providing for an optimum dispersion of the PCM(s) throughout the dispersing polymer.

10 Granules of the above-described PCM/dispersion polymer are then melt blended with a high molecular weight polymer in order to produce concentrate pellets of the invention that contain about 15 weight percent of the PCM(s).

15 This high molecular weight polymer is selected for its affinity for the low molecular weight polymer and for the physical qualities that are desired of articles (i.e., fibers and the like) that are extruded, or melt spun in conventional manners using the concentrate pellets of the invention.

The foregoing and other features, utilities and advantages of the invention will be apparent from the following description of preferred embodiments of the invention.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

20 In accordance with the present invention, a process is disclosed for making concentrate pellets of one or more polymers, each pellet having one or more PCMs therein, the concentrate pellets being adapted for use in extrusion and melt spun manufacturing processes.

25 The concentrate pellet manufacturing process of this invention provides benefits that are achieved by adding PCMs to products that are manufactured using extrusion processes such as the melt spun process, non-limiting examples

being fibers such as nylon fibers, polyester fibers, polyethylene fibers and polypropylene fibers, films, and injection molded articles.

The present invention forms concentrate pellets having enhanced reversible thermal properties, which concentrate pellets can then be used to make temperature regulating articles having PCMs therein, the melt spun fiber manufacturing process being an example.

The PCMs of the invention can be in a microencapsulated form wherein a hollow capsule or hollow shell having a diameter of from about 1 to about 3 microns protects the PCMs that are within the capsule/shell from exposure to the high temperature and high shear processing that is commonly found in the manufacture of melt spun fibers and melt spun fiber components.

The PCMs of the invention can be contained within, surrounded by, or encapsulated within a number of polymer matrix formats, or within carrier polymers, to thereby provide for the ease of handling of the PCMs, while at the same time, offering a degree of protection to the PCMs from the harsh environment of the extrusion/melt spin processing the PCM-containing concentrate pellets, as well as protecting the PCMs that are within melt spun fibers from subsequent fiber processing.

In accordance with the invention, raw or not-capsulated PCMs can be incorporated into a process by which the concentrate pellets of the invention are manufactured. In this case, the PCMs are preferably introduced into the concentrate pellet manufacturing process via one of the late pellet manufacturing steps, to thereby minimize exposure of the PCMs to high temperature processing.

In one example of the invention, the PCMs are incorporated into any of the many process steps by which the concentrate pellets are manufactured.

In another example, a wetflush process is used to form a plurality of plastic-based granules, each granule containing mPCMs. Preferably,

approximately 50 weight percent of a selected mPCM is placed in a compatibilizer plastic, and the PCM/plastic mixture is then ground down to form a plurality of granules, each granule containing mPCM. After the granules are formed, concentrate pellets are formed from the mPCM granules  
5 by adding a virgin thermoplastic polymer, to thereby reduce the mPCM concentration within the finished concentrate pellet product. In one example, the resulting concentrate pellets included about 15 weight percent mPCM in relation to the thermoplastic polymer.

In accordance with a feature of the invention, the above-described  
10 compatibilizer plastic is a low molecular weight dispersing polymer, and the above-described virgin thermoplastic polymer is a high molecular weight polymer, the low molecular weight dispersing polymer being selected for its compatibility with, and for its affinity for, the mPCM, and the virgin thermoplastic polymer being selected for its affinity for the low molecular  
15 weight polymer and for the physical qualities that are desired of articles that are extruded or melt spun in conventional manners using the concentrate pellets of the invention.

Upon formation of concentrate pellets of the invention, the concentrate pellets can be extruded/melt spun as is (for example, to produce monofilament  
20 fibers that contain about 15 weight percent of the mPCM), or the concentrate pellets can be blended with another polymer(s) and then extruded/melt spun, for example, to produce multi component fibers having, for example, from about 5 to about 10 weight percent of the mPCM.

Finally, upon the formation of the PCM containing individual fibers as  
25 above described, a desired fiber material, fabric material or textile material is formed. As described above, the individual fibers can then be used to manufacture a non-woven material, or the fibers can be used by way of a yarn spinning process to manufacture fabric or textile materials using a weaving process, a knitting process, or the like. It is understood that the

fiber/fabric/textile material that is manufactured from the fibers is a matter of choice, and is not critical to this invention. The manufactured fiber/fabric/textile material will contain the above- described PCM, and as a result will exhibit thermal regulatory properties.

5           It should also be noted that the above-described concentrate pellet manufacturing process is applicable to raw or un-encapsulated PCMs, wherein the PCM is placed into the concentrate pellets and the concentrate pellets are then passed through an extrusion or melt-spun manufacturing process to form extruded/melt spun articles such as fibers having the PCM contained or held  
10       within a plurality of isolated volumes or spaces that are dispersed throughout the article.

          In accordance with embodiments of the present invention, concentrate pellets can be manufactured using a variety of manufacturing processes; for example, 1) the use of mPCM containment systems, 2) the use of gelled  
15       containment PCM systems, 3) the use of alternative containment PCM systems, or 4) the addition of non-contained, raw or non-micro-encapsulated PCM systems.

          One such process for use with mPCMs involves wet flushing and/or subsequent compounding of the mPCM into a thermoplastic polymer matrix or  
20       carrier. In one example, wet flushing consisted of the addition of a dispersing-polymer into a heated mixing bowl and then melting the polymer. Preferably, but without limitation thereto, the dispersing-polymer was a low molecular weight polymer. Upon melting of the dispersing-polymer, mPCM wet cake was slowly added to the molten polymer and permitted to disperse as, at the  
25       same time, water was flashed or flushed off. Upon completion of the dispersion and the removal of water, the dispersed mPCM/polymer concentrate was removed, cooled, and thereafter chopped into granules of acceptable dimensions for later blending.

The above-described dispersing polymer may include graft, homo, or copolymers of polyolefins, polyamides, polyesters, or other thermoplastic polymers that are compatible with, and have an affinity for, the final polymer matrix of the melt extruded concentrate pellet product, which final polymer matrix is preferably a high molecular weight polymer matrix.

The above-described mPCM wet cake may consist of between about 1 and 90 weight percent solids in water, and preferably contains between about 60 and 70 weight percent solids. Final concentrations of the mPCM in the wet cake concentrate can be from about 30 to about 60 weight percent, and preferably it is from about 45 to about 55 weight percent.

To insure improved mixing in the final extruded concentrate pellet product, the wet flush concentrate can be further blended into the finished product polymer matrix, to yield a concentrate pellet containing mPCM of about 10 to about 30% weight percent, and preferably about 15 weight percent.

PCMs can be gelled, absorbed or physically contained in a number of ways. One such means of gelling or physical containment is by the addition of silica particles, fumed silica particles, zeolite particles or absorbent polymers to the PCM to provide for ease of addition to the above-described dispersing polymer.

PCMs that are physically contained can then be manufactured into concentrate pellets in a manner similar to the above-described process. One preferred method is by removing the above-described wet flushing step and simply blending the PCMs with the dispersing-polymer, or with the final matrix polymer of the concentrate pellet when the concentrate pellet is extruded. This process yields concentrate pellets with PCM concentrations similar to those described above; for example, from about 5 to about 70 weight percent, and preferably about 15 weight percent.



PCMs that are not micro-encapsulated or otherwise contained can also be processed into concentrate pellets via the liquid injection of the PCM into the concentrate pellet melt extrusion process, or by the co-feeding of solid PCM with the concentrate pellet's dispersing-polymer.

5           Liquid PCM can be thoroughly filtered and mixed to insure homogeneity prior to injection. Liquid injection of the PCM can occur at any time in the pellet melt extrusion process, but preferably it occurs as late in the process as is possible in order to insure adequate mixing and in order to minimize exposure of the PCM to high temperature. By using this late-stage PCM  
10 addition method, exposure of the PCM to high temperatures and to any subsequent degradation or loss of PCM is reduced.

          Solid PCM can be processed into concentrate pellets by simply co-feeding the solid PCM and the pellet dispersing or matrix polymer resin into the feed throat of the pellet melt extruder. Solid PCMs can also be side stuffed  
15 into the pellet melt extruder in order to prevent feed throat plugging.

          The above processes yield concentrate pellets having PCM concentrations in about the 5 to 70% weight percent range, and preferably in about the 15 to 25% weight percent range.

          This invention provides temperature regulating benefits that are  
20 achieved by adding PCMs to synthetic articles such as fibers, films, foams and injection-molded members, which articles that are made by extrusion processes of which the melt spin manufacturing of fibers is a non-limiting example.

          In accordance with this invention, at least one water-based PCM is added to a melted dispersing-polymer that has an affinity for the PCM. For  
25 example, if the PCM comprises a plurality of individual PCM volumes, with each volume encased within a shell (i.e., a mPCM), then the dispersing polymer is selected so as to have an affinity for the material of which the shells are formed.

As this first melt is heated, the PCM is uniformly dispersed throughout the first melt, and the water is driven off of the first melt. Upon cooling, the resulting solid is mechanically processed, such as by pulverizing, to form granules that contain the PCM.

5 A second polymer, which can be called a matrix polymer, is then melted, and the above-mentioned granules are added to this second melt. This second polymer can be called an article-specific polymer since it is selected to have an affinity for the dispersing-polymer, and to also have physical properties that are desirable for the final extruded article.

10 Upon cooling of this second melt, the resulting solid is processes to form concentrate pellets. These concentrate pellets are then usable to form synthetic articles such as fibers, films, foams and injection-molded devices by way of an extrusion processes; for example, synthetic fibers are made by way of a melt spin process.

15 A variety of polymers, homopolymers, copolymers or blends of the polymers can be used as the matrix polymer. Non-limiting examples of such matrix polymers are (1) polyamides such as Nylon 6, Nylon 6/6, Nylon 12, polyaspartic acid, polyglutamic acid; (2) polyamines; (3) polyimides; (4) polyacrylics such as polyacrylamide, polyacrylonitrile, and esters of  
20 methacrylic acid and acrylic acid; (5) polycarbonates such as polybisphenol A carbonate, and polypropylene carbonate; (6) polydienes such as polybutadiene, polyisoprene, and polynorbornene; (7) polyepoxides; (8) polyesters such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polycaprolactone, polyglycolide, polylactide,  
25 polyhydroxybutyrate, polyhydroxyvalerate, polyethylene adipate, polybutylene adipate and polypropylene succinate; (9) polyethers such as polyethylene glycol (polyethylene oxide), polybutylene glycol, polypropylene oxide, polyoxymethylene (paraformaldehyde), polytetramethylene ether

(polytetrahydrofuran), polyepichlorohydrin; (10) polyfluorocarbons; (11) formaldehyde polymers such as urea-formaldehyde, melamine-formaldehyde, and phenol formaldehyde; (12) natural polymers such as cellulose, chitosans, lignins, and waxes; (13) polyolefins such as polyethylene, polypropylene, 5 polybutylene, polybutene, polyoctene; (14) polyphenylenes such as polyphenylene oxide, polyphenylene sulfide and polyphenylene ether sulfone; (15) silicon containing polymers such as polydimethyl siloxane, and polycarbomethyl silane; (16) polyurethanes; (17) polyvinyls such as polyvinyl butryal, polyvinyl alcohol, polyvinyl acetate, polystyrene, polymethylstyrene, 10 polyvinyl chloride, polyvinyl pyrrolidone, polymethyl vinyl ether, polyethyl vinyl ether, polyvinyl methyl ketone; (18) polyacetals; and (19) polyarylates.

The PCM may be dispersed in a variety of dispersing polymeric materials. Non-limiting examples of these dispersing polymers include those listed above, they may be homopolymers or copolymers, and they may vary in 15 molecular weight, functionality, and polymer chain architecture. Non-limiting examples include homopolymers of polyethylene, polypropylene, Nylon 12, polybutylene terephthalate, and copolymers such as polyethylene-co-vinyl acetate, polyethylene -co-acrylic acid, polybutylene terephthalate-co-polytetramethylene terephthalate, and polylauryllactam-block- 20 polytetrahydrofuran.

High or low molecular weight materials may be used with lower molecular weight polymers being preferred for the dispersing polymer.

The functionality of the polymers can also be varied; for example, with the addition of amine, amide, carboxyl, hydroxyl, esters, ethers, epoxide, 25 anhydrides, isocyanates, silanes, ketones, and aldehydes.

The polymer architecture may also be varied, examples being homopolymers, copolymers, linear polymers, branched polymers, block polymers, star polymers, comb polymers, dendritic polymers, graft copolymers and other combinations where branch arms or grafts may be the same or a

different homopolymer or copolymer, and branch arms or grafts may be added in a controlled or a random manner.

Example 1:

As an example, about 5.0 pounds of a low molecular weight  
 5 polyethylene homopolymer (A-C16 polyethylene, drop point of 102°C,  
 manufactured by Honeywell Specialty Chemical) was added to a wet flushing  
 apparatus, and the homopolymer was then slowly melted and mixed at from  
 about 110 to about 130°C. Once the entire homopolymer was melted, about  
 8.47 pounds of a mPCM wet cake (micro PCM lot# M42-31, 59.0% solids,  
 10 manufactured by MicroTek Laboratories, Inc.) was slowly added to the molten  
 homopolymer over about a 30 minute time period.

Water was flashed off as the mPCM disperse within the homopolymer.  
 Mixing of the dispersion continued until less than about 0.15 weight percent of  
 the water remained (as measured using Karl-Fischer titration). The dispersion  
 15 was then cooled and chopped for further processing, the chopped granules  
 contained about 50 weight percent mPCM.

Melt spinnable concentrate pellets were then manufactured by dry  
 blending about 30-pounds of the above-described granules with about 70-  
 pounds of a high molecular weight fiber grade polypropylene thermoplastic  
 20 resin (Polypropylene homopolymer 6852 from PB Amoco Polymers).

The resulting dry blend was then extruded using a 2 ½-inch single screw  
 extruder with all zones set at about 230-degrees C, with a screw speed of  
 about 70 rpm, with 150 mesh screens, and with a nitrogen purge, thus  
 producing concentrate pellets of the invention.

The above-extruded extrudable/melt spinable concentrate pellets were then oven-dried overnight at about 50-degrees C and at about 1 mm Hg of vacuum.

5 The concentrate pellets containing about 15 weight percent of mPCM, were then extruded/melt spun at temperatures between about 230 and 265-degrees C, and preferably at about 235 to 245-degrees C.

Filaments were spun/wound at takeup speeds of up to about 1600 meters per minute (mpm), and yielded from about 20 to about 6 deniers per filament of melt spun fibers having a temperature regulating characteristic with  
10 reversible thermal storage properties as was provided by the mPCM. Using Differential Scanning Calorimeter (DSC) testing, these fibers provided between about 17.5 and 23.2 J/g of thermal energy storage capacity.

#### DSC Testing and Analysis:

Differential Scanning Calorimeter (DSC) measurements of the above  
15 fibers were made using a Perkin Elmer Pyris 1 instrument. Cooling was accomplished using a FTS Systems Intercooler 1. Data analysis was performed using a Perkin Elmer Pyris Thermal Analysis System and Software for Windows, version 3.72.

Test samples were prepared in Perkin Elmer hermetically sealed  
20 aluminum sample pans, and testing was performed while the test samples were continuously subjected to N<sub>2</sub> flow.

Test conditions consisted of 1) cooling the test samples to about minus 10-degrees C, followed by 2) isothermal hold for about 1 minute at minus 10-degrees C, and 3) heating from minus 10-degrees C to about 50-degrees C at a  
25 rate of about 5-degrees C per minute, followed by 4) isothermal hold for about 1 minute at 50-degrees C, and then 5) cooling from 50-degrees C to about minus 10-degrees C at a rate of about 5-degrees C per minute.

While the methods disclosed herein have been described with reference to particular steps performed in a particular order, it will be understood that these steps may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the present invention.

- 5 Accordingly, unless specifically indicated herein, the order and grouping of the steps is not a limitation of the present invention.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various other changes in form and detail may be made  
10 without departing from the spirit and scope of the invention.

What is claimed is: